Emerging Technologies for Treating Contaminants in Marine Wastewater

Compass Water Solutions
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Bilge Samples Processed by CWWS

	Average, ppm	Range	Heli–Sep Ave. Efficiency %
TDS	18000	960-38000	39
TSS	887	40-16240	59
TO&G	1100	20-46400	68
C6	ND	378-200	
C10	225	1-7905	72
C22		4-17840	
Fe	14	1.4-43.4	42
COD		70-11000	
BOD		5-1500	

Oil Water Separation (OWS)

- Emulsion breaking or demulsification is the separation of the dispersed oil droplet from the continuous water phase. All chemical and mechanical methods of demulsification conform to Stoke's law:

$V = [\ 2(\rho_o - \rho_w)\ g\ R^2\ ] / [9\mu]$

V = oil droplet rise velocity

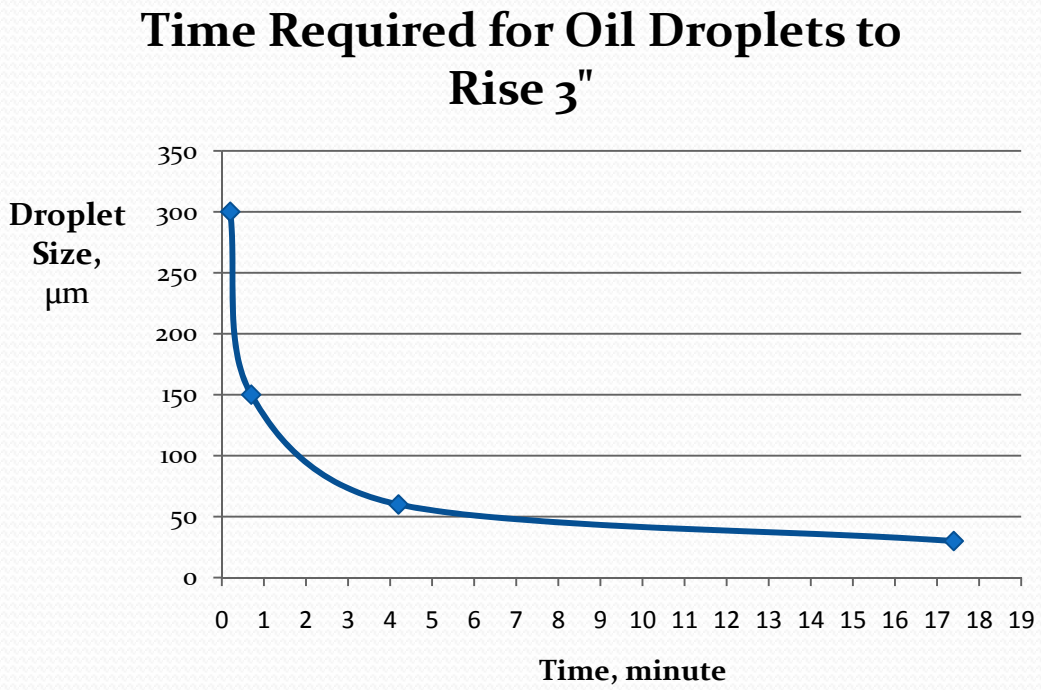
$\rho_o - \rho_w$ = Oil -water density differential

R = Mean radius of oil droplets

μ = Water viscosity

OWS Efficiency

- OWS is proportional to square of radius. A small change in oil droplet size can increase significantly OWS efficiency



General OWS technologies

Oil Types	Size, µm	Removal methods
Free Oil (FOG)	150+	Skimming
Mech. emulsified oil High shear pump, mixers	20-150	Coalescent Media DAF, IAF
Chem. emulsified oil Soap, surfactants	<20	Emulsion breakers, Plus coalescent media
Dissolved oil, i.e. benzene, phenols, xylene,…	<2	GAC, membrane, absorbants
Oil wet solids, i.e. sediments, wastewater particulates	Thin film on solids	Filter press, organoclay, Sand filter
*G.R. Alther, Biomin Inc.		

How Particle Size Colors Emulsions

Particle size (µm)	Emulsion appearance
Macro globules >150 µm	Droplets may be visibly distinguished
10 µm-100µm	Milky white emulsion
1.0µm-10µm	Bluish-white emulsion
0.05µm-1µm	Smoky gray, semitransparent
<0.05	Transparent micro emulsion

Emulsion Breaking

- Emulsions can be classified into mechanical and chemical emulsions.
- Mechanical emulsions are created through the process of pumping, large pressure drops through chokes and control valves.
- Chemical emulsions are stabilized by surfactants added in the industrial process
- Gravity separation primarily affects free oil.
- Chemically emulsified oils need to be destabilized to liberate free oil so that the oil will separate by gravity or flotation.
- Once the emulsion is broken, the same removal techniques applicable to free oil can be utilized.

Mechanical Demulsification

- Sometimes heating the emulsion to 160 ^{o}F followed by several hours of settling would break the poorly emulsified oils.
- Coalecent Media
- Dissolved Air Flotation (DAF); Water is supersaturated with pressurized air, then metered to the flotation chamber. Air bubles, 30µ-120 µ in size, are formed which coalesce with oil and dirt as they rises through the chamber. Solids and oils can be skimmed off the surface.
- Induced Air Flotation (IAF): Compression air is sparged through the chamber bottom. Air bubbles up to 1000 µ coalesce with oil and dirt on the way to the top. They form a froth layer which can be skimmed off. IAF is less efficient than DAF, but can remove more sand and grit particles.
- Ultrasound

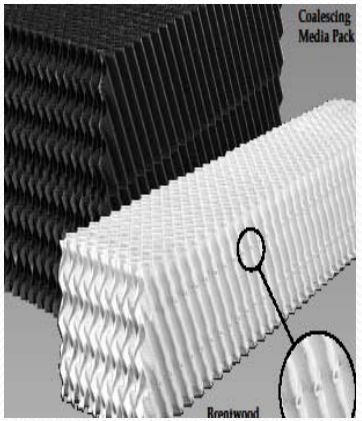
Coalescence Media

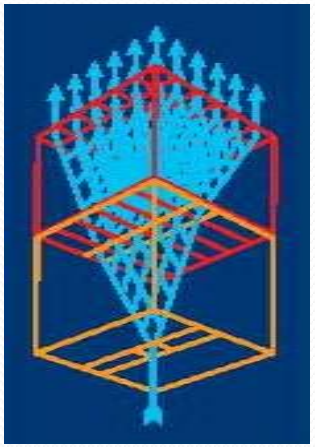
- Oil emulsion is composed of a continuous phase (water) and a discontinuous phase (oil droplets).
- The droplet size decrease with higher mixing energy and lower interfacial tension
- Detergent promotes the formation of emulsion by lowering the interfacial tension
- The coalescent matrix (CM) has surface properties that is not only hydrophobic but also oleophilic. As the oil droplets contact the CM surface, a new CM-oil interface is preferred to oil-water interface. Oil droplets adhere to the CM surface.
- As the population of oil droplets adhere to the CM surface increases, the crowding factor causes the droplets to annex each other . Droplets tend to grow bigger in sizes.

Coalescence Media

Brentwood CM has cross-hatched channels at angles about 60° to vertical.

HD-QPAC has higher surface area/volume. Water passes at 90° to verticle.



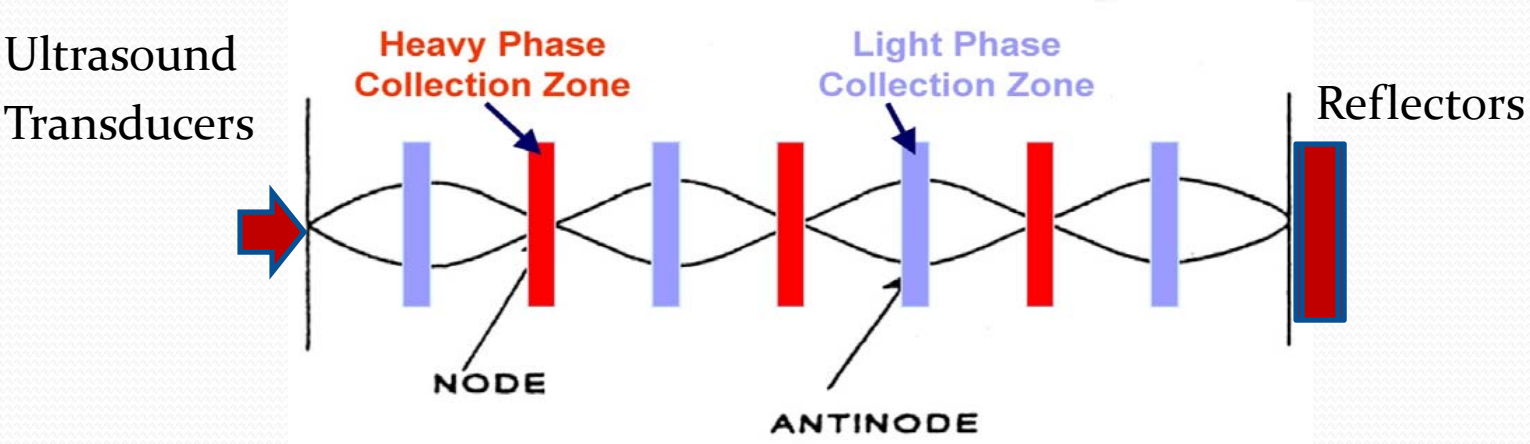


Evolutionary Steps to Improve OWS

- Higher surface area per matrix volume
- Shorter rising distance for oil droplets
- Enhanced oil absorbing surface for matrix
- Simplification of matrix chamber to reduce plugging
- Optimize flow paths, volume, oil removal frequency,…

Oil Emulsion Breaking & Coalescing by Ultrasound

- Ultrasonic separation utilizes acoustic standing wave



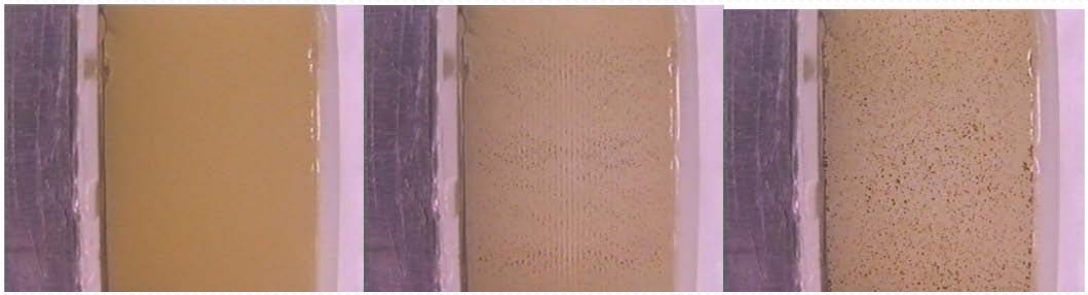
- Forms parallel stationary pressure nodal planes
- Act as Coalescence Zones

Non-intrusive, robust, no pressure requirements

Ultrasound (US) Oil Coalescer*

- 20mm cells with transducer attached to the left hand side
- Oil droplets grew from 10 µm to ~1mm in 5-10 seconds, view from above

0 sec., US on | 5 sec., US off | 5-10 sec, US off



* Sinker, A. Produced Water Society, Houston, 2007

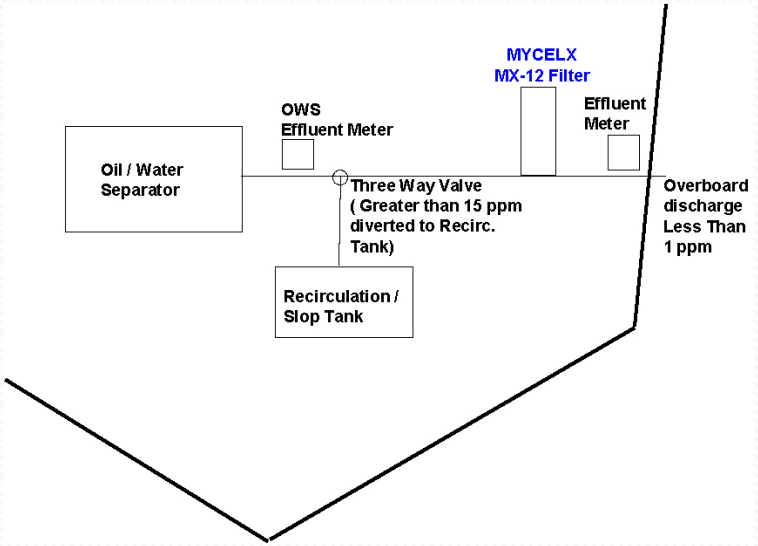
Process Conditions for Different Flotation Processes

Flotation process	Air flow $l.m^{-3}$ water	Size of bubbles	Input power Wh/m^3	Est. Retention time, min	Hydraulic surface loading mh^{-1}
Macro air flotation (grease removal)	100-400	2-5 mm	5-10	5-15	10-30
IAF (froth flotation)	10.000	0.1-2 mm	60-120	4-16	
DAF (clarification)	15-50	40-70 µm	40-80	20-40 (excluding flocculation)	3-10

Chemical Demulsification

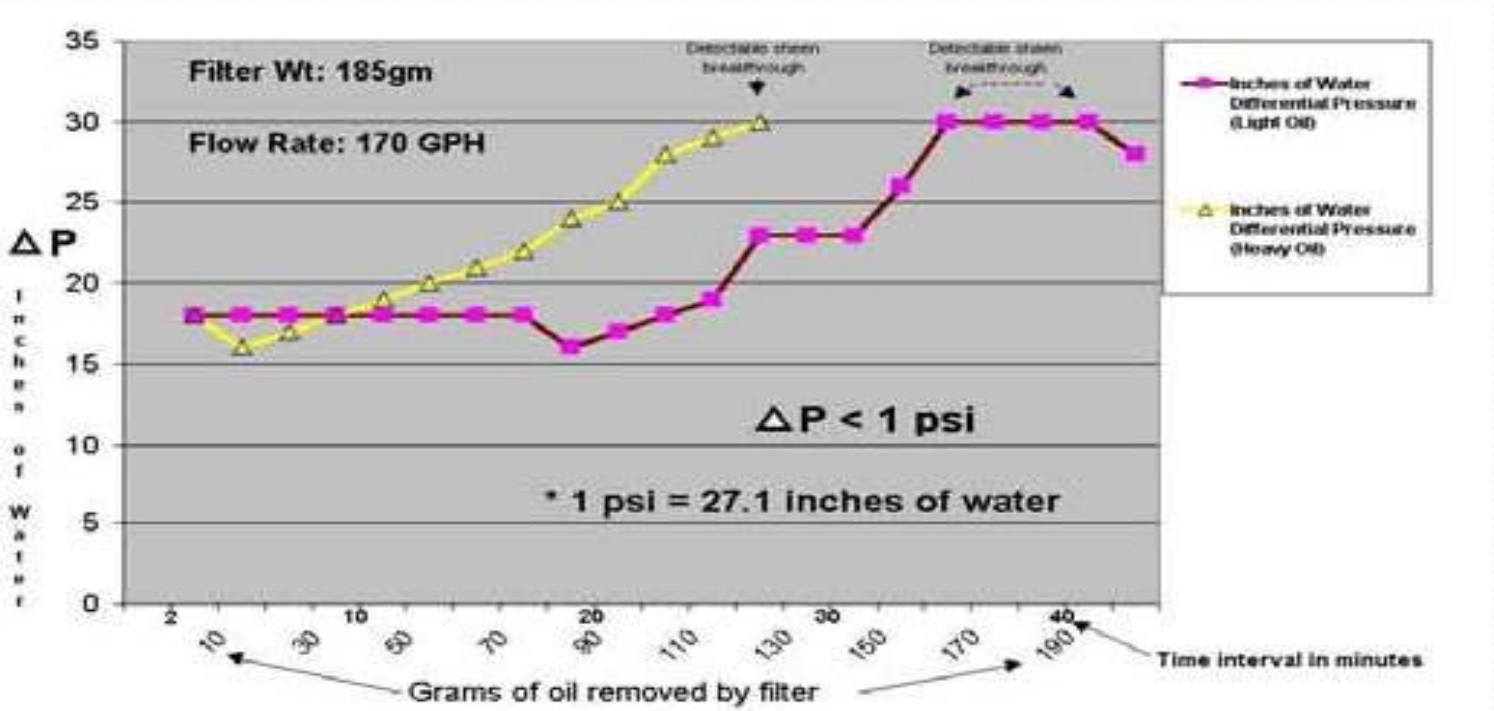
- Emulsified oil can have anionic (-) or cationic (+) surface charges depending on the kind of detergents or surfactants. Most oil emulsions have anionic surface charges. Neutralization of the surface charges breaks the emulsion.
- Calcium or magnesium salt can be added to emulsion stabilized by sodium soap. Emulsion is broken when Ca^{++} and Mg^{++} replace Na^{+} in the soap.
- Other inorganic demulsifiers are ferric and aluminum chlorides. They lowers water pH and break the emulsion.
- Aluminum sulphate adds ionic strength and modifies surface charges.
- Significant amount of sludges are produced.
- Alcohol or acetone break emulsion by dissolving and removing emulsifiers from the oil phase

MycelX Oil Filter For Bilge Water



- Polymer synthesized by linseed oil and methyl methacrylate (US Pat 6491822)
- Absorb emulsified oil up to 65% of filter media weight using 5µ MF
- Flow rated unaffected by degree of oil saturation
- Claimed to be lower cost than membrane filter

Coalescent Assisted Filtration



ΔP vs. % Saturation

JOWA EBU

Norwegian-made Emulsion Breaking Unit

0.33 m^3/hr-1.33 m^3/hr Batch operation

Solid demulsified agents and NaOH are used to break the emulsions. Claimed 80% removal of emulsified oil.

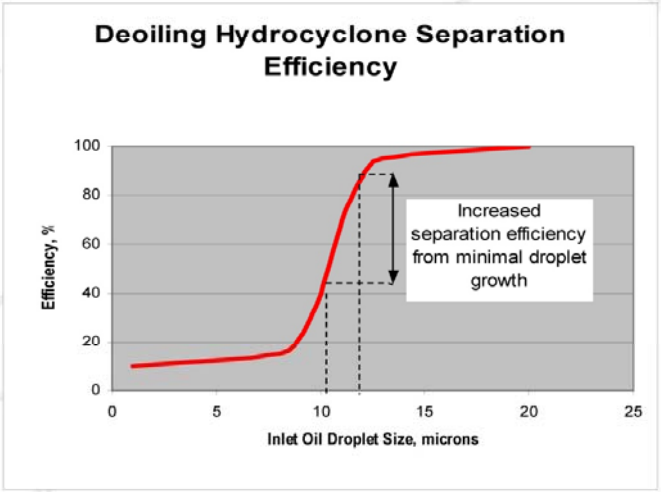
The 1m^3/hr unit costs about $50K. About 200 units were sold internationally

Oil Coalescing using HydroCyclone

Influent: 500 ppm oil; Effluent: 60 ppm; Effluent = 20 ppm if inlet is packed with PECT-F fiber media

PECT-F®

Cyclotech

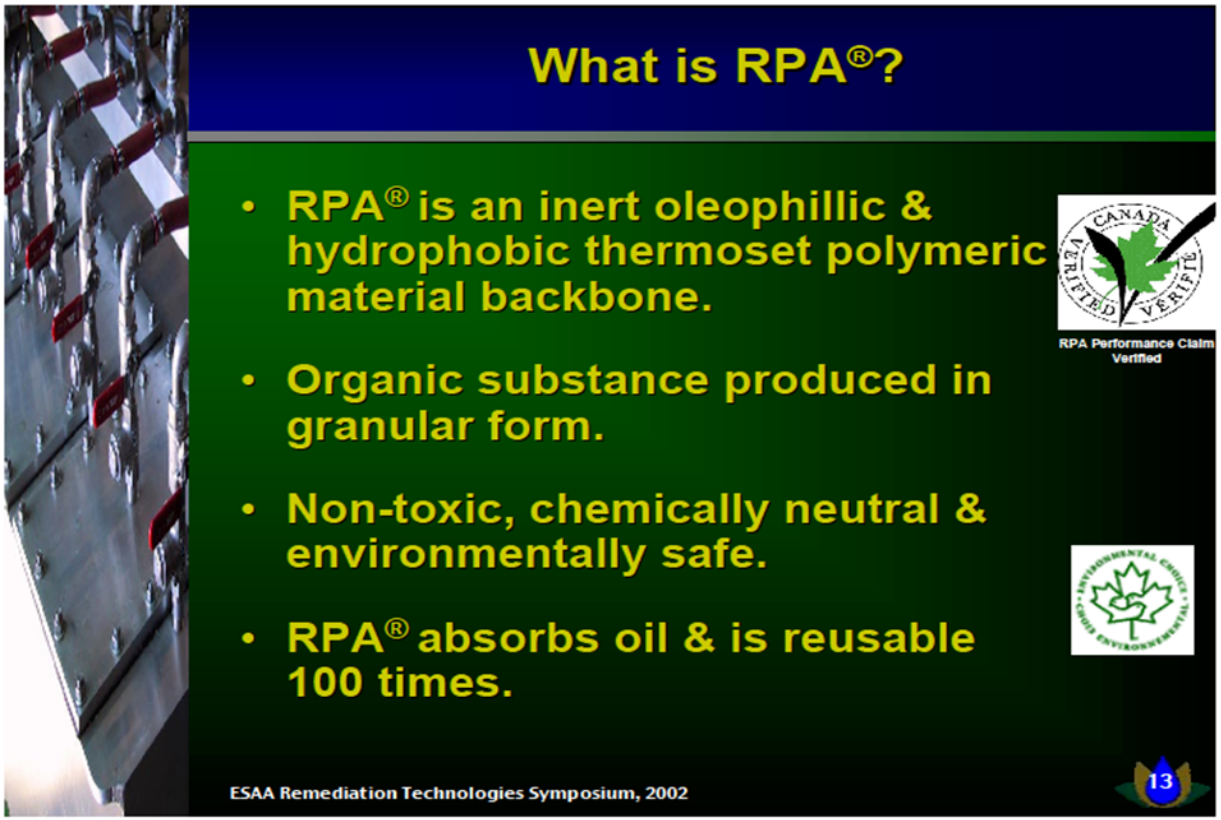


Separasjonsteknologi 2007, Stavanger

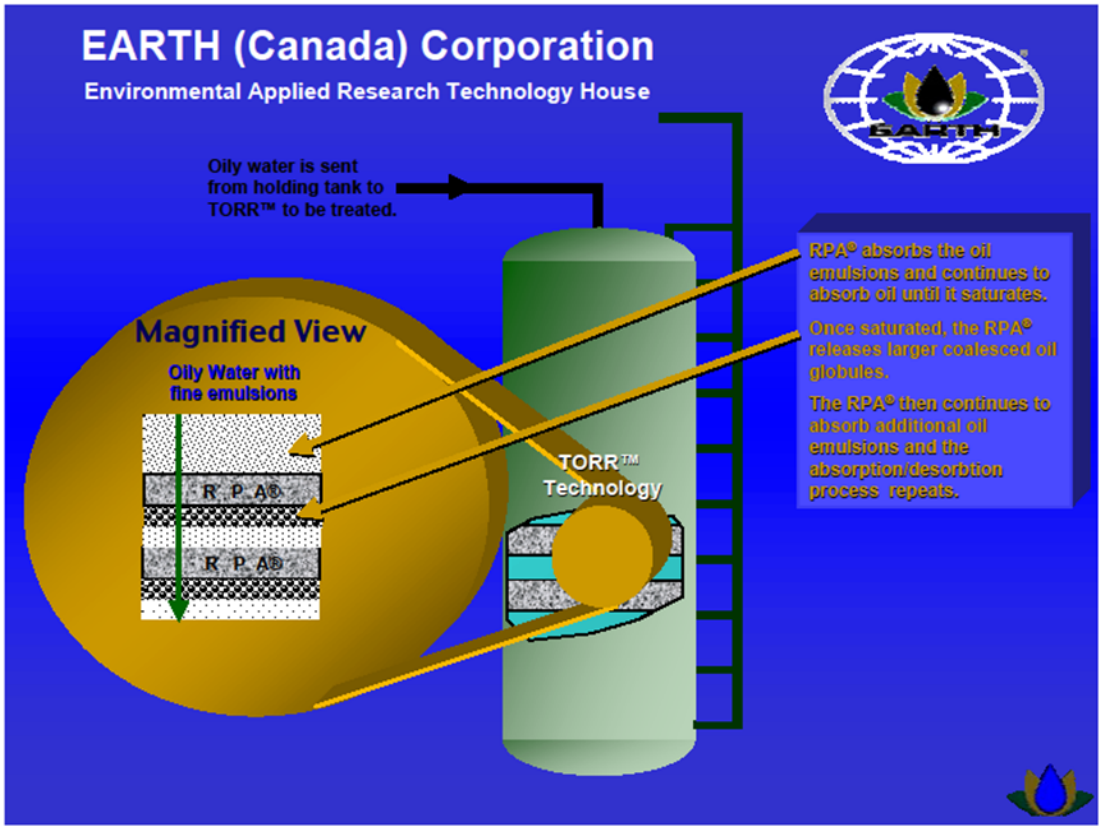
Marinfloc

- Emulsion breaking using forced flotation & flocculant
- Pretreat the MEPC 60(33) OWS system
- Effluent < 15ppm oil
- 1 m^3/hr is currently available ; the 2 m^3/hr will be available soon

Reusable Petroleum Absorbent



Earth Canada TORR Process



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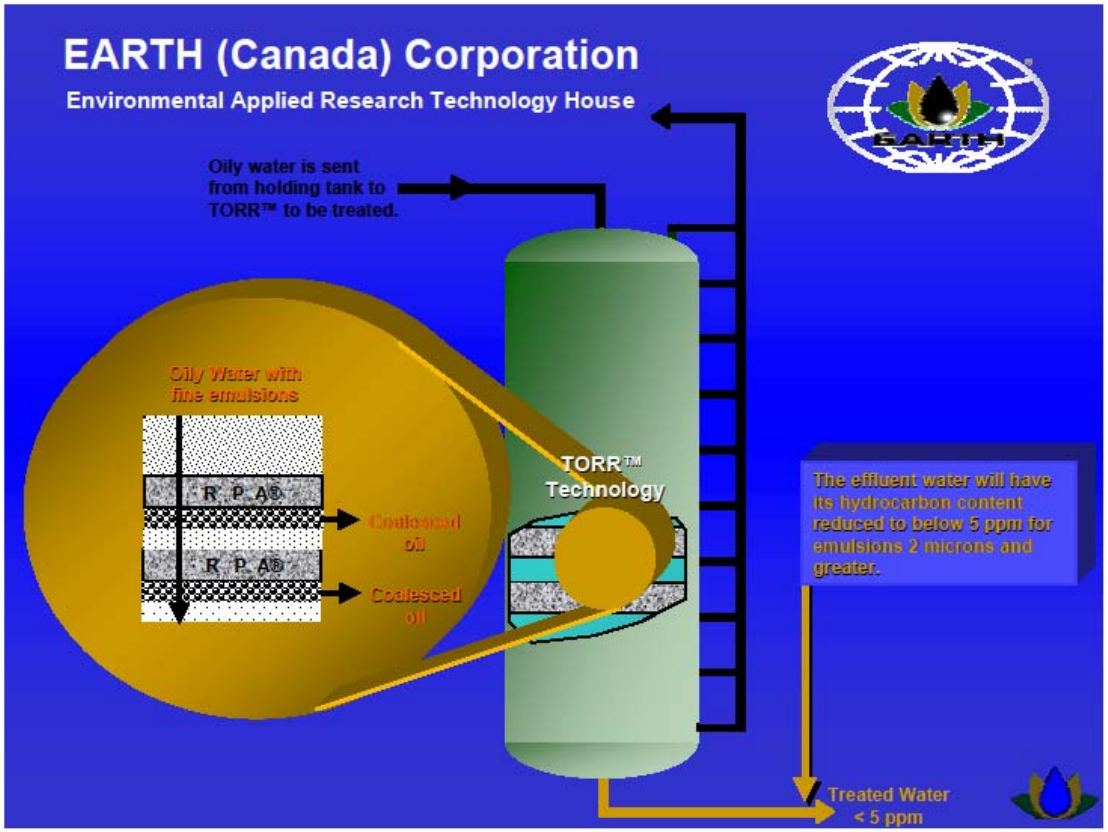

Biological Oxidation

- Ensolve may be the first system to be adapted for marine application under the trade name PetroLiminator
- Reducing oil, free & emulsified to 1ppm-2ppm using natural occurring bacteria.
- The key modification for marine application is the use of a matrix affixed with oil-scavenging bacterial to prevent washout.
- Some high-strength oily-bilge can cause system upsets .
- May need advance chemical oxidation to enhance bio-oxidation

Membrane BioReactor (MBR)

- Hamworthy KSE membrane bioreactor (HKSE MBR) is aerobic reactor which use a special membrane to increase the biomass concentration to 20 g/l.
- The membrane uses 8mm bore tubes mounted into 200 mm fiber casing to create a UF filter with low TMP.
- HKSE MBR is IMO/USCG certified
- HKSE MBR is less efficient for synthetic grease and tar.
- Some toxic oil ingredients can cause system upsets.

Ballast Water Treatment

- The BalPure relies on oxidized halide ions in sea water to destroy inorganic and organic matters in ballast water.
  - Oxidizers is generated in an proprietary electrolyzer
  - Residual oxidizers are neutralized before treated ballast water is released.
- The OceanGuard Ballast Water Management System (Qingdao Headway Tech. Co) utilizes AOP to quickly purify ballast water
  - Hydroxyl free radicals is produced by ultrasound and electrocatalysis
  - The system is self-cleaning to purge the organism in the cells.
  - OceanGuard can be used in both rivers and oceans